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PATENT SPECIFICATION

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- (21) Application No. 52501/71 (22) Filed 13 Feb. 1974
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 (72) Inventors MASAOKI TAKIMOTO and SATORU HONJO



(54) METHOD OF TONING ELECTROPHOTOGRAPHIC
 PHOTOSENSITIVE MATERIAL

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ERRATA

SPECIFICATION No. 1,376,343

55

Page 2, lines 66 and 92, for adsorption read
 absorption

Page 2, line 104, for difference read dif-
 ferences

Page 4, line 5, for monocyamine read mero-
 cyanine

60

Page 4, line 115, for employ- read employable

Page 5, line 23, for 0.001 read 0.0001

Page 5, line 112, for an read and

Page 7, line 59, for (0.2 read (0.02

65

Page 8, line 96, after bleaching insert is

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25 an ordinary paper sheet, said colour signi-
 ficantly affects the image quality finally ob-
 tained if the process does not contain such
 transfer step. When using such photoconductive
 30 powdered material, however, spectral sensitiz-
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 35 finally obtained and the spectral sensitivity of
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 conductive powdered material various dyes
 are known, such as xanthene dyes, triphenyl
 methane dyes, azo dyes, cyanine dyes, and
 40 merocyanine dyes.

Such spectral sensitizing dyes undergo fad-
 ing at different rates when the electrophoto-
 graphic photosensitive layer is exposed to light.
 Consequently if the colour of the photosensi-
 45 tive layer is selected to make a compromise
 with the spectral sensitivity directly after the
 developing treatment, decoloration or fading

severely restricted depending upon the pigment
 used as the toner or the resin component em-
 ployed in the developer.

Thus the object of this invention is to
 provide a simplified process for toning the
 electrophotographic photosensitive layer after
 the developing treatment thereof.

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Another object of this invention is to pro-
 vide an improved electrophotographic photo-
 sensitive layer prepared so as to make the
 toning thereof as simple as possible after the
 developing treatment.

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According to the invention there is provided
 a method for toning an electrophotographic
 photosensitive layer essentially consisting of
 photoconductive powdered material, a resin-
 ous binder and two or more sensitizing dyes
 of different absorption rate variation (as herein
 defined) which comprises selectively bleaching
 said dyes after developing a toner image on
 said layer.

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The selective bleaching of colouring material
 contained in the electrophotographic photo-

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[Price 25p]

SEE ERRATA SLIP ATTACHED

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(54) METHOD OF TONING ELECTROPHOTOGRAPHIC
 PHOTOSENSITIVE MATERIAL

(71) We, FUJI PHOTO FILM CO., LTD., a Japanese Company, of No. 210, Nakanuma, Minami Ashigara-Machi, Ashigara-Kamigun, Kanagawa, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for toning a coloured electrophotographic photosensitive layer after a developing treatment is applied thereon.

It is already known that an electrophotographic photo-sensitive layer can be produced by dispersing photoconductive powdered material into a resinous binder, and for this purpose various photoconductive materials are already known to be usable such as cadmium sulphide, zinc oxide and zinc sulphide. Although the colour of the electrophotographic photosensitive layer is not an important factor in electrophotographic processes which include the step of transferring the toner image onto an ordinary paper sheet, said colour significantly affects the image quality finally obtained if the process does not contain such transfer step. When using such photoconductive powdered material, however, spectral sensitizing dyes are frequently added in order to correct spectral sensitivity or to improve sensitivity. Consequently it has been necessary in preparing a photosensitive layer to make a suitable compromise between the image quality finally obtained and the spectral sensitivity of such layer. For spectral sensitization of photoconductive powdered material various dyes are known, such as xanthene dyes, triphenyl methane dyes, azo dyes, cyanine dyes, and merocyanine dyes.

Such spectral sensitizing dyes undergo fading at different rates when the electrophotographic photosensitive layer is exposed to light. Consequently if the colour of the photosensitive layer is selected to make a compromise with the spectral sensitivity directly after the developing treatment, decoloration or fading

of said photosensitive layer after a certain time may result in a disagreeable colour. However, in case of storing the unused electrophotographic photosensitive layer in a dark place, it is possible to obtain a fairly long storage life even when it is sensitized with cyanine dyes which generally show very poor stability against light. This fact eventually leads to careless selection of sensitizing dyes without consideration of the light-fastness thereof, and it is thus made impossible to maintain the final image quality at a constant level for a prolonged period. In order to prevent this drawback it has been proposed to remove the sensitizing dye from the electrophotographic photosensitive layer after the developing treatment thereof, such as by a bleaching bath consisting of a solution of organic acid, as disclosed in United States Patent Specification No. 3,250,614. The bleaching bath employed in such process should, however, be such as to leave said photosensitive layer and the image intact, and therefore the composition of the bath is severely restricted depending upon the pigment used as the toner or the resin component employed in the developer.

Thus the object of this invention is to provide a simplified process for toning the electrophotographic photosensitive layer after the developing treatment thereof.

Another object of this invention is to provide an improved electrophotographic photosensitive layer prepared so as to make the toning thereof as simple as possible after the developing treatment.

According to the invention there is provided a method for toning an electrophotographic photosensitive layer essentially consisting of photoconductive powdered material, a resinous binder and two or more sensitizing dyes of different absorption rate variation (as herein defined) which comprises selectively bleaching said dyes after developing a toner image on said layer.

The selective bleaching of colouring material contained in the electrophotographic photo-

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sensitive layer after the developing treatment, which is an essential step of the process according to this invention, can be conveniently carried out by irradiation with strong light, particularly ultraviolet light, by treatment in an acidic or alkaline bleaching bath, or by treatment with peroxide compounds. This bleaching step may also accomplish, simultaneously, other functions or operations such as washing, drying, fixing of the toner holding image, or formation of a surface protective layer on said layer in addition to said bleaching operation. It is known to fix and protect such image by applying a transparent lacquer to the surface of the electrophotographic photosensitive layer, and this invention can be carried out very simply and effectively by adding a very small amount of peroxide to such transparent lacquer. In this case it is of course necessary to include both (a) colouring materials capable of being easily bleached by such peroxide present in said lacquer and (b) those relatively stable against said peroxide, in a suitable ratio in the electrophotographic photosensitive layer.

Fixing and surface protection of the image can also be performed by laminating a transparent plastics film onto the surface of the electrophotographic photosensitive layer after the developing treatment, for example in the manner claimed in our copending Application No. 50523/71 (Serial No. 1,361,670), and similar effects can be obtained if a peroxide is included in the adhesive material employed in the lamination.

The electrophotographic photosensitive layer employed in the reproduction is adjusted to a neutral colour by means of sensitizing dyes or by toning agents, and it is generally preferred for it to have, after the developing treatment, a bluish or greenish colour rather than a yellowish or pinkish colour. Consequently it is preferable to incorporate into the photosensitive layer a colouring material of a yellow or pink colour with a relatively low stability against light or chemical agents and also one of blue or green colour with relatively high stability.

In spite of such preference, however, it is possible to bleach any colour selectively by

the choice of colouring materials with suitable stability to be added to the electrophotographic photosensitive layer, for example in order to meet personal taste or to classify the images by the colour of subject or of background.

The colouring materials to be used in the electrophotographic photosensitive layer in the method of the present invention are classified into the following three groups (a), (b) and (c).

(a) Colouring material having a high fading rate, that is, having poor resistance to light:

This group includes materials which have an adsorption rate variation (as hereinafter defined) of 15% or more, and examples include cyanine dyes such as 3,3'-di- β -carboxyethyl-thiacarbocyanine bromide and merocyanine dyes such as 3-carboxymethyl-5-[(3-ethoxycarbonylmethyl - 2(3H) - thiazolinilidene)ethylidene]rhodamine.

(b) Colouring material having a low fading ratio, that is, having good light resistance:

This group includes materials which have an absorption rate variation (as hereinafter defined) of 3% or less and examples include phthalocyanine dyes such as Direct Blue 86, azo dyes such as Acid Red 27, anthraquinone dyes such as Acid Green 25, inorganic pigments such as cadmium sulphide, and organic pigments such as phthalocyanine pigments (e.g. Pigment Blue 15), quinacridone pigments (e.g. Pigment Violet 19) and azo pigments (e.g. Pigment Red 57 or Pigment Yellow 12).

(c) Colouring material having fading rates intermediate between the high fading rate of (a) and the low fading rate of (b), that is materials which have a normal light resistance:

This group includes materials which have an adsorption rate variation (as hereinafter defined) of 3 to 15% and examples include triphenyl methane dyes such as Acid Blue 9, xanthene dyes such as Acid Red 87 and sulphone phthalein dyes such as dibromo dichloro phenol sulphone phthalein.

The absorption rate variation is defined by the following equation:

$$\text{absorption rate variation} = \frac{(\text{initial absorption rate}) - (\text{absorption rate after being exposed to direct light for 2 hours})}{(\text{initial absorption rate})}$$

In this equation, the "absorption rate" is the peak value of the absorption of the colouring material.

The difference between the light-resistance of the said colouring materials in groups (a), (b) and (c) are particularly marked in the

presence of peroxides.

It is preferable that the photosensitive layer formed by the method of this invention has a colouring material of the group (c) providing the main spectral sensitizing effect and hence the background colour of the layer and has

the colouring materials of the other groups (a) and (b) complementing the said effect.

In a photosensitive layer in which the background colour is adjusted by the action of the colouring material of the group (c) and the spectral sensitivity is complemented by that of the group (a), rapid bleaching or toning of the colouring material of the group (a) produces an electrophotographic photosensitive material which has high sensitivity and has finally the desired colour.

When the background colour is adjusted by the action of the colouring material of the group (c) and the spectral sensitivity is complemented by that of the group (b), it is, of course, also possible to impart a spectral sensitizing effect and, in addition, to change the background colour to the specific and desired colour. That is, even if the colouring material of the group (c) is toned in the toning process after the developing treatment, the background colouring is retained since the colouring material of the group (b) remains.

It is also possible, of course, to use the colouring material of each of the groups (a), (b) and (c) at the same time in order to adjust the colouring.

An electrophotographic photosensitive material was prepared having an electrophotosensitive layer which consisted of 100 parts by weight of zinc oxide, 12 parts by weight of a styrenated alkyd resin (marketed by Japan Reichhold Co. as Styresol No. 4400; "Styresol" is a registered Trade Mark), 8 parts by weight of a 50% solution in xylene of a polyisocyanate (marketed by Bayer AG. as Desmodur L; of acid value below 8; "Desmodur" is a registered Trade Mark), 80 parts by weight of *n*-butyl acetate and 0.03 part by weight of a colouring material as shown in the following table and the amount of variation of the spectral absorption by light irradiation was measured in each case to determine the absorption rate variation thereof in the manner defined above.

| Class of colouring material | Name of colouring material | Absorption rate c variation (%) | Corresponding group according to absorption rate [(a), (b) or (c)] |
|-----------------------------|---|---------------------------------|--|
| cyanine dye | 3,3'-di- β -carboxy-ethyl-thiacarbocyanine bromide | 30 | (a) |
| merocyanine dye | 3-carboxymethyl-5-[(3-ethoxy-carbonylmethyl-2(3H)-thiazolinilidene)-ethylidene]-rhodanine | 18 | (a) |
| phthalocyanine pigment | Pigment Blue 15 | 0 | (b) |
| quinacridone pigment | Pigment Violet 19 | 0 | (b) |
| azo pigment | Pigment Red 57 | 1 | (b) |
| azo pigment | Pigment Yellow 12 | 0 | (b) |
| inorganic pigment | Cadmium sulphide | 0 | (b) |
| azo dye | Acid Red 27 | 2 | (b) |
| anthraquinone dye | Acid Green 25 | 2 | (b) |
| phthalocyanine dye | Direct Blue 86 | 1 | (b) |
| triphenyl-methane dye | Acid Blue 9 | 10 | (c) |
| xanthene dye | Acid Red 87 | 9 | (c) |
| sulphone-phthalein dye | Dibromo dichloro phenol-sulphone-phthalein | 10 | (c) |

The above results confirm that the groups of the colouring materials, as used in this invention, are efficiently classified according to the respective absorption rate variation

thereof. The specific examples of dyes and pigments illustrated hereinbefore are ones which are classified according to the structures thereof; colouring materials which have similar

structures show almost the same value of the absorption rate variation, and hence are also classified in the respective groups (a), (b) and (c).

- 5 For example, cyanine or monocyamine dyes can be subjected to toning according to this invention because of their relatively low light-fastness or relatively low stability against peroxides in comparison with xanthene or azo dyes. An electrophotographic photosensitive layer can be prepared in a neutral colour by regulating the amount of fluorescein and rose bengal (which are xanthene dyes) and brilliant blue FCF (a triphenylmethane dye). To such photosensitive layer there is further added a cyanine dye in order to improve its spectral sensitivity, and a transparent lacquer containing a peroxide is applied after the developing treatment in order to fix the reproduced image and to protect the surface of the layer. Successive exposure to light causes selective bleaching of cyanine to provide a reproduction with a background of nearly neutral colour, which remains unchanged with gradual increase of brightness even under prolonged exposure to light.

- For certain purposes it is preferred that the photosensitive layer should have almost the same sensitivities to blue, to green and to red light. In such case it is necessary to increase the sensitivity of said layer in the blue and green wavelength regions when a tungsten lamp is to be used as the light source for exposure, and such modification inevitably results in a reddish colour in said layer. This red colouration can be compensated for by adding a dye and/or pigment capable of absorbing red light but incapable of spectral sensitization in the electrophotographic process, but such addition not only lowers significantly the brightness of said photosensitive layer but also reduces the efficiency of sensitizing dye in the red wavelength region. According to this invention, on the other hand, the above-mentioned drawback can be removed by employing sensitizing dyes of distinctly different fading rates for the red region and blue-green regions and also by employing the dyes for the latter regions in relatively large amounts. More specifically the method of this invention can be realized by using cyanine or merocyanine dyes for sensitization in the blue and green regions and relatively stable phthalocyanine dyes for the red region, and applying an acrylic lacquer containing a peroxide for surface protection.

- Furthermore the resinous binder in the electrophotographic photosensitive layer may turn to yellow due to photocatalytic activity of the photoconductive material, e.g. zinc oxide. Such drawback should naturally be suppressed most desirably by the improvement of said resin itself, but, according to this invention, it is possible to maintain the background constantly at a neutral colour by pre-

viously adding a phthalocyanine dye in said photosensitive layer in combination with other colouring materials. Although the bleaching step according to this invention can be accomplished by various methods as mentioned above, the use as aforesaid of a transparent lacquer containing peroxide or of a transparent laminate film containing a peroxide in the adhesive material therefor has marked advantages as explained above, enabling to fix and protect the obtained image at the same time.

Said transparent lacquer can be composed, for example, as follows, in parts by weight:

| | | |
|---|----------|----|
| Styrene butyl methacrylate copolymer (50:50) | 2 parts | 80 |
| Daiflon S-2 (CCl ₂ F—CCl ₂ F, Daikin Kogyo Co., Ltd.) | 40 parts | |
| Cyclohexane | 40 parts | |
| Mineral spirit (solvent naphtha) | 15 parts | 85 |
| n-butyl acetate | 5 parts | |

Since a styrene-butyl methacrylate copolymer usually contains benzoyl peroxide in an amount of ca. 0.1% as the polymerization initiator, the transparent lacquer thus obtained also contains residual peroxide in an amount of ca. 0.01%. It is however desirable to add further benzoyl peroxide to the lacquer for use in the method of this invention. Also in the case of using the acrylic resin obtained by employing azobisisobutyronitrile as the polymerization initiator, similar results can be achieved by adding a small amount of benzoyl peroxide or other organic peroxide to said transparent lacquer.

An example of the adhesive material used for laminating the transparent film is given in United States Patent Specification No. 3,381,596 and has the following composition in parts by weight:

| | | | |
|---|-----------|------------|-------|
| Ethyl acrylate | 55 parts) | terpolymer | |
| N-vinyl-2-pyrrolidone | 20 parts) | | 90 |
| N-tert-butylacrylamide | 25 parts) | | parts |
| Low molecular weight epoxy resin (bisphenol-A-epichlorohydrin condensate) | | 9.9 parts | 110 |
| Citric acid | | 0.1 parts | |
| Peroxide | | 0.08 parts | |

The above-mentioned U.S. Patent 3,381,596 also discloses examples of peroxides employed in such formulation, and particularly suitable peroxides are hydroperoxides, such as hydrogen peroxide, tert-butyl hydroperoxide, cumene hydroperoxide, 2,5-dimethylhexyl-2,5-dihydroperoxide and p-menthane hydroperoxide.

The adhesive material for laminating said film can be of the type which is semi-liquid at room temperature or of the heat-sensitive type which is solid at room temperature. An efficient laminating method consists of lamin-

ating a plastics film provided with a layer of an adhesive material which is solid at room temperature and soluble in a non-polar liquid employed in the liquid developing process while the photosensitive layer is still wet with said non-polar liquid after developing with liquid developer, and according to this invention a small amount of organic peroxide is added to said adhesive layer.

The material constituting the reproduced toner image is required to be stable against the reagent (e.g. organic peroxide) used for decomposing the sensitizing dyes. Most organic and inorganic pigments, including carbon black, remain intact in the presence of a small amount of such peroxides and can therefore be satisfactorily employed as toner in the process of this invention unless such pigment is excessively susceptible to oxidation.

The amount of said organic peroxide in said adhesive material layer provided on the plastics film or in transparent lacquer can be within the range of 0.001—0.1 gram/m² photosensitive layer, preferably 0.0001—0.1 gram/m². An amount above these ranges does not lead to any additional advantage. The peroxide is presumed to have a catalytic action and is frequently capable of decomposing dyes to an extent greater than its chemically equivalent amount.

Where a bleaching bath is used, this may be a solution of an acid or alkali in an organic solvent; potassium hydroxide is a suitable alkali. The bleached layer can be covered with a protective layer.

The accompanying drawing shows the formulae in Figs. 1 and 2, of dyes used respectively in the Examples 2 and 5 below.

This invention will be illustrated by the following examples. All parts are by weight.

EXAMPLE 1.

The following components were mixed together:

- 100 parts of zinc oxide
- 12 parts of a styrenated alkyd resin (marketed by Japan Reichhold Company under the trade mark Styresol No. 4400)
- 8 parts of a polyisocyanate (marketed by Bayer AG under the name Desmandur L; "Desmondur" is a registered Trade Mark) as the hardener and
- 80 parts of *n*-butyl acetate;

the mixture was blended in a porcelain ball mill for 15 hours to obtain a white suspension.

The white suspension thus prepared was divided into four samples, three of which were subjected to sensitizing treatment by addition of one of the following three dye solutions.

Sample A (Control).

No dye addition.

Sample B.

To the suspension were added 4 mg of fluorescein, 4 mg of Rose Bengal, 2 mg of Bromochlorophenol Blue and 3 mg of 3,3'-di- β -carboxyethylthiadibenzocyanine bromide dissolved in 10 ml of methanol, with respect to 100 g of the zinc oxide.

Sample C.

To the suspension were added 3 mg of fluorescein, 3 mg of Rose Bengal and 4 mg of Brilliant Blue FCF (C.I. 42090) dissolved in 10 ml of methanol, with respect to 100 g of the zinc oxide.

Sample D.

To the suspension were added the solution used in sample C further containing 2 mg of 3,3'-di- β -carboxyethylthiadibenzocyanine bromide.

The suspensions were each mixed in a homogenizer, and then each sample was coated to a dry coating thickness of 10 microns on a support material consisting of art paper previously subjected to surface treatment with colloidal alumina (marketed by Nissan Chemical Company under the trade name Alumina Sol No. 100) to render the paper electroconductive. After drying, each coated paper was placed in a thermostat box at 50° C for 12 hours to harden the resinous binder to provide electrophotographic material.

The relative photosensitivities of the above samples under a tungsten lamp of ca. 3000° K were:

$$A:B:C:D = 1:20:10:18.$$

The photosensitive layers prepared with the above-mentioned samples were uniformly electrostatically charged and imagewise exposed, and they provided excellent reproduced images on development with a liquid developer containing particles of carbon black toner in an insulating liquid.

Subsequently each of the toner images was coated, to fix and protect it, with a layer about 10 microns thick of an acrylic lacquer which was essentially composed of a styrene butyl methacrylate copolymer (50:50) and contained ca. 0.01% (by weight of the copolymer) of benzoyl peroxide which had been added as the polymerization initiator.

The C.I.E. coordinates (defining the colours of the layers) were determined for each sample with an without lacquer and also after exposure for 2 hours to sun light and fluorescent light of an intensity of about 500 lux; the results are shown in Table 1.

TABLE 1

| | | C.I.E. coordinates: | | | |
|--------|------------|---|--|--|--|
| Sample | Coordinate | (1) of fresh photo- sensitive layer | (2) directly after lacquering | (3) after light- exposure for 2 hours without lacquering | (4) after light- exposure for 2 hours after lacquering |
| A | x | 0.3099 | 0.3109 | 0.3099 | 0.3125 |
| | y | 0.3175 | 0.3187 | 0.3173 | 0.3205 |
| B | x | 0.3057 | 0.3109 | 0.3075 | 0.3128 |
| | y | 0.3104 | 0.3139 | 0.3118 | 0.3159 |
| C | x | 0.3081 | 0.3074 | 0.3086 | 0.3090 |
| | y | 0.3157 | 0.3183 | 0.3165 | 0.3185 |
| D | x | 0.3032 | 0.3029 | 0.3046 | 0.3091 |
| | y | 0.3123 | 0.3142 | 0.3137 | 0.3161 |

The lacquering caused colour changes in the background area. Fading or bleaching was accelerated by lacquer coating as is clearly indicated by the difference between the measurement conditions (2) and (4) larger than that between (1) and (3) in Table 1. The sample B was found to be closest directly after lacquer coating (condition (2)) to the colour of standard C light source, which is represented by $x = 0.3100$ and $y = 0.3160$. On the other hand the samples C and D were designed to become closest to the colour of standard C light source after a certain period after lacquer coating (condition (4)). The colour of sample B was found to be distinctly reddish compared with the C light source at the condition (4), principally because of rapid decomposition of the 3,3'-di- β -carboxyethylthiadibocyanine bromide.

The advantages of this invention are most clearly found in the sample D, which was designed to show high sensitivity and residual colour very close to that of standard C light source. In this example, in order to improve photosensitivity while retaining satisfactory residual colour of the sample C, 3,3'-di- β -carboxyethylthiadibocyanine bromide was added to the photosensitive layer and this dye was decomposed rapidly after development by means of the peroxide in the acrylic lacquer.

EXAMPLE 2.

To the undyed white zinc oxide suspension described in Example 1 was added a dye solution of the following composition, per 100 g of zinc oxide:

Sample E.

| | |
|--|--------|
| Fluorescein | 3.0 mg |
| Rose Bengal | 3.0 mg |
| C.I. Direct Blue 86 (C.I. 74180; formula shown in Figure 1 of the drawing) | 5.0 mg |
| Methanol | 10 ml |

the resultant dyed mixture was homogenized and coated on an art paper sheet previously subjected to electroconductive treatment so as to obtain a dry coating thickness of 10 microns. The photosensitive layer thus prepared showed spectral absorptions at 510, 580 and 680 m μ and a photosensitivity about 15 times higher than that of sample A in Example 1.

The material was coated with the lacquer containing benzoyl peroxide described in Example 1, and then exposed to tungsten light for two hours; this exposure significantly reduced the spectral adsorption at 510 and 580 m μ , while the absorption at 680 m μ remained almost unchanged to provide a somewhat bluish photosensitive layer. This change is attributable to the higher stability of Direct Blue 86 against peroxides compared with fluorescein and Rose Bengal.

After light exposure for 5 hours, the only observable spectral absorption was that of Direct Blue 86 and the photosensitive layer changed to pale blue.

EXAMPLE 3.

The following ingredients were mixed together:

- 100 parts by weight of zinc oxide
 12 parts by weight of styrenated alkyl resin
 8 parts by weight of polyisocyanate compound as hardener and
 5 80 parts by weight of *n*-butyl acetate.

The mixture was divided into three samples to each of which was added one of the following colouring materials and the sample was then blended for 16 hours in a porcelain ball mill to obtain suspensions coloured pale yellow, pink and blue respectively.

| | | parts by weight |
|-------------|----------------------|--------------------|
| Sample F | Cadmium sulphide | 0.003 |
| 15 Sample G | Brilliant Carmine 6B | 0.003 |
| Sample H | Phthalocyanine Blue | 0.003 |

To each of the suspensions thus prepared were respectively added the dye solution employed for sample D in Example 1, well mixed and coated on an art paper sheet previously subjected to electroconductive treatment so as to obtain a dry coating thickness of 10 microns. After drying, the coated paper was placed in a thermostat box at 50° C for 16 hours to harden the resinous binder.

The photosensitive layers (samples F, G and H) were developed with a liquid developer containing carbon black as toner and then dipped for 30 seconds in a bleaching bath of the following composition at 25° C:

| | |
|-------------------------|--------|
| 30 Methyl alcohol | 300 ml |
| Ethyl alcohol | 300 ml |
| Acetone | 300 ml |
| <i>n</i> -Butyl acetate | 100 ml |
| 35 Potassium hydroxide | 10 g |

The sensitizing dyes were completely removed from the samples F, G and H to provide reproductions with a black image on a background of pale yellow, pink and blue, respectively.

Successively the photosensitive layers were washed with methyl alcohol, then dried and coated with the acrylic lacquer of Example 1 for surface protection to provide reproductions which were easily classifiable by the colour of their background.

EXAMPLE 4.

The samples B, C and D in Example 1, sample E in Example 2, and samples F, G and H in Example 3 were laminated with a plastics film by means of an adhesive material containing peroxide.

The plastics film employed for laminating was composed of polyethylene terephthalate film provided with a layer of adhesive material essentially consisting of a terpolymer of ethyl acrylate, *N*-vinyl-2-pyrrolidone and *N*-tert-butylacrylamide and containing a small amount (0.2 wt.% with respect to resin) of tert-butyl hydroperoxide, and the lamination was carried out by means of a heated roll.

In the samples B, C, D and E, exposure to light for 5 hours provided similar results as shown before, while the samples F, G and H each had an appearance similar to that described in Example 3 after light-exposure for ca. 2 hours.

EXAMPLE 5.

Instead of the sample D in Example 1 which was found to be unsuitable for multi-colour reproduction because of its unbalanced spectral sensitivity under a tungsten lamp light source, the following combination of dyes was employed. The photosensitive layer prepared was reddish in the fresh state, but the background of reproduction changed to a neutral colour after light-exposure for 2 hours after coating with lacquer containing peroxide.

In this example a dye solution of the following composition was added to the suspension, per 100 g of zinc oxide.

Sample I.

| | | |
|--|-------|----|
| 3-β-carboxyethyl-2(3,3-dicyano-allylidene) benzothiazole | 20 mg | |
| Rose Bengal | 10 mg | 85 |
| C.I. Direct Blue (C.I. 74180) | 5 mg | |
| Methanol | 10 ml | |

The ordinary electrophotographic procedure consisting of electrostatic charging, imagewise exposure and developing was repeated three times with exposure of a multi-colour original image through blue, green and red filters respectively. The development was carried out with three liquid developers respectively containing (1) a yellow pigment of the formula shown in Figure 2 of the accompanying drawing to obtain a yellow image, (2) quinacridone magenta to obtain a magenta image and (3) phthalocyanine blue to obtain a cyan image. After development, the photosensitive layer was coated with a transparent lacquer which contained polyisobutyl methacrylate and butyl acetate as solvent and benzoyl peroxide in an amount of 0.1 wt.% with respect to the methacrylate.

Thus, according to this invention, it is made possible to obtain electrophotographic photosensitive material free from the drawback resulting from the uneven spectral sensitivity at the repeated exposures and capable of showing a neutral residual colour after development.

EXAMPLE 6.

The photosensitive layer described in Example 2 was laminated with a polypropylene film provided with an adhesive layer consisting of:

| | | |
|---|--|-----|
| 80 parts of polybutyl methacrylate | | |
| 20 parts of an aliphatic polyester (marketed by the Japan Reichhold Company under the trade name D-tite 307 MH) | | 120 |
| 0.005 part dicumyl peroxide and | | |
| 0.005 part of benzoyl peroxide. | | |

The lamination was effected by passing the photosensitive sheet and said film between rolls heated to 70° C, after said photosensitive sheet had been developed with an isoparaffinic liquid developer containing carbon black toner and then washed with an isoparaffinic solvent free from said toner and while said sheet was still wet with said solvent.

After lamination the photosensitive layer showed gradual change of colour to show blue background finally.

WHAT WE CLAIM IS:—

1. A method of toning an electrophotographic photosensitive layer essentially consisting of a mixture of a powdered photoconductive material, a resinous binder and two or more sensitizing dyes of different absorption rate variation (as hereinbefore defined), which comprises selectively bleaching said dyes after developing a toner image on said layer.
2. A method as claimed in Claim 1, wherein said two or more sensitizing dyes are selected from at least two of the following groups: (a) dyes having an absorption rate variation of 15% or more; (b) dyes having an absorption rate of from 3% or less and (c) dyes having an absorption rate of between 3 and 15%.
3. A method as claimed in Claim 2, wherein one or more dyes selected from group (c) provides the main spectral sensitization in the photosensitive layer, and one or more dyes selected from group (a) and/or group (b) complement said main sensitization.
4. A method as claimed in Claim 2 or 3, wherein said dyes of group (a) are cyanine and merocyanine dyes.
5. A method as claimed in any of Claims 2 to 4, wherein said dyes of group (b) are phthalocyanine dyes, azo dyes, anthraquinone dyes, inorganic pigments, phthalocyanine pigments, quinacridone pigments and azo pigments.
6. A method as claimed in any of Claims 2 to 5, wherein said dyes of group (c) are triphenylmethane dyes, xanthene dyes and sulphonaphthalein dyes.
7. A method as claimed in any of Claims 2 to 6, wherein said dye of group (a) is selected from 3,3'-di- β -carboxyethylthiacarbo-cyanine bromide and 3-carboxymethyl-5-[(3-ethoxycarbonylmethyl - 2(3H) - thiazolinilidene)ethylidene]rhodanine.
8. A method as claimed in any of Claims 2 to 7, wherein said dye of group (b) is selected from Acid Red 27, Acid Green 25,

Direct Blue 86, cadmium sulphide, Pigment Blue 15, Pigment Violet 19, Pigment Red 57 and Pigment Yellow 12.

9. A method as claimed in any of Claims 2 to 8, wherein said dye of group (c) is selected from Acid Blue 9, Acid Red 87 and dibromo, dichloro-phenolsulphonaphthalein.

10. A method as claimed in any preceding claim, wherein the bleaching is effected by treating the material with an organic or inorganic peroxide.

11. A method as claimed in Claim 10, wherein the peroxide is contained in a transparent acrylic lacquer which is coated over the image-bearing surface.

12. A method as claimed in Claim 11, wherein the lacquer contains a copolymer of styrene and butyl methacrylate.

13. A method as claimed in Claim 11 or 12, wherein the peroxide is present in the acrylic lacquer as residual polymerization initiator for the acrylic polymer in the lacquer.

14. A method as claimed in Claim 12 or 13, wherein the peroxide is benzoyl peroxide.

15. A method as claimed in Claim 10, wherein the peroxide is contained in the adhesive layer of an adhesive plastics film which is laminated to the image-bearing surface.

16. A method as claimed in any of Claims 10 to 15, wherein the peroxide is selected from hydroperoxide, hydrogen peroxide, tert-butyl hydroperoxide, cumene hydroperoxide, 2,5-dimethylhexyl-2,5-dihydroperoxide and *p*-menthane hydroperoxide.

17. A method as claimed in any of Claims 10 to 16, wherein the amount of the peroxide applied is 0.0001 to 0.1 gram per metre of the surface of the photosensitive layer.

18. A method as claimed in any of Claims 1 to 9, wherein the bleaching effected by treatment in an alkaline or acidic bleaching solution.

19. A method as claimed in any of Claims 1 to 9, wherein the bleaching is effected by irradiation of the image-bearing surface with light.

20. A method as claimed in any preceding claim, wherein an electrostatic latent image on the layer is developed with a liquid developer containing carbon black as toner.

21. A method of toning an electrophotographic layer as claimed in Claim 1, substantially as hereinbefore described with reference to any of the foregoing Examples.

22. An electrophotographic material when treated by the method claimed in any preceding claim.

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FIG. 1

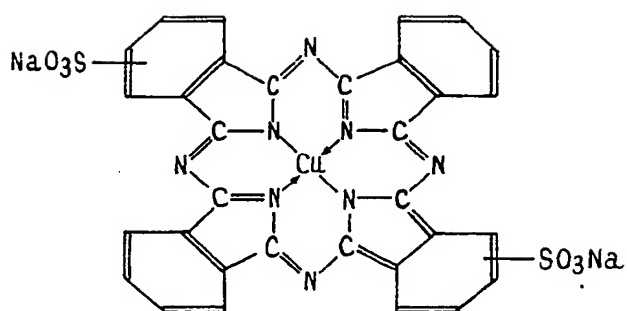
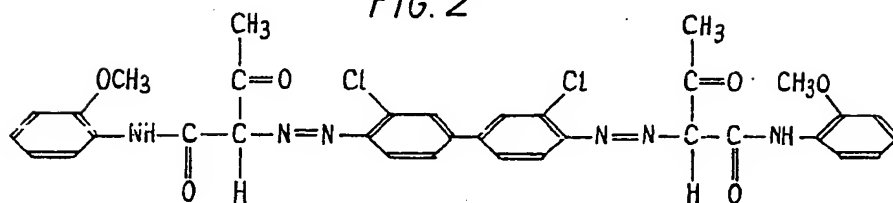


FIG. 2



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